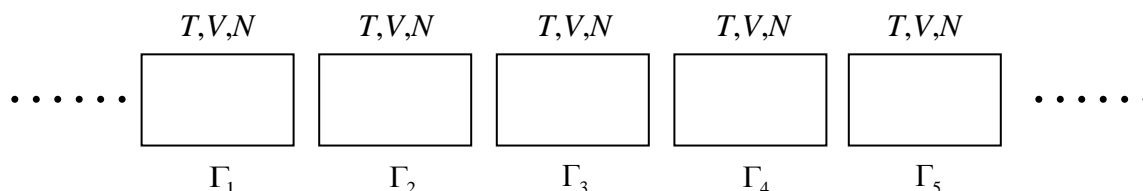


CHEM 371: Lecture 4

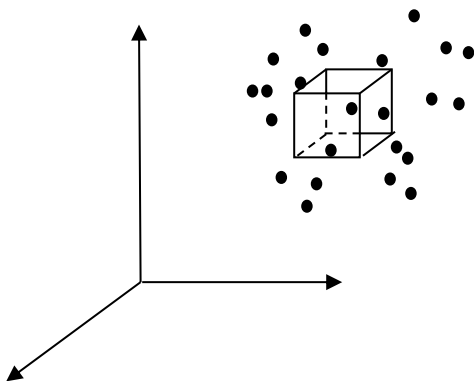
The 1-d harmonic oscillator is one of the few systems for which the phase space trajectory can be worked out in complete detail. We can't expect to do likewise for an N particle system in 3-d, which would involve finding the solutions to $6N$ coupled differential equations, an essentially impossible task. We can at best, therefore, hope to develop a *statistical* description of the system's dynamics, which means doing no more than stating how likely the system is to be in some microstate at time t , if it had started out in some other microstate at time 0. But how do we do even this?

The answer is to adopt Gibbs's ensemble approach, which focuses not on the single thermodynamic system of interest, but on a large collection of *replicas* of this system, each one of which at some instant of time t is *macroscopically* identical to every other, but is generally different from them microscopically. Thus, if the given system were prepared at certain values of, say, T , V and N , every other member of the ensemble would share exactly the same values of these parameters, but they would, in general, occupy different microstates. The figure below is a schematic sketch of a few of the replicas in such a system:



where $\Gamma_i = \{\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N\}$, $i = 1, 2, \dots, M$. Because the ensemble is large (i.e., $M \gg 1$), it contains a distribution of microstates, meaning at a given time t some number of all the microstates are in one particular microstate, some other number are in another microstate, and so on for all the systems in the ensemble.

Consider this ensemble in phase space. Schematically, it might look something like this at some instant of time:



The box in the middle of the figure represents a hypercube in phase space; its volume is

$\prod_{i=1}^N \prod_{\alpha} dp_{i\alpha} dq_{i\alpha} \equiv d\mathbf{p}^N d\mathbf{q}^N$, and at that instant of time it contains some number of the

members of the ensemble. Let's assume the box is located at the phase point $\Gamma = \{\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N\} \equiv \{\mathbf{q}^N, \mathbf{p}^N\}$, where the *density* of phase points is $\rho = \rho(\mathbf{q}^N, \mathbf{p}^N, t)$. If dn denotes the *number* of phase points in the given volume (assumed to be small, hence the infinitesimal notation), we have the relation

$$dn = \rho(\mathbf{q}^N, \mathbf{p}^N, t) d\mathbf{q}^N d\mathbf{p}^N \quad (1)$$

and if we added up these numbers in all such volume elements, we'd find that $\int \rho(\mathbf{q}^N, \mathbf{p}^N, t) d\mathbf{q}^N d\mathbf{p}^N = M$. Since M is a number that we can't really fix (we only know it has to be large), it's convenient at this point to introduce the function $f(\mathbf{q}^N, \mathbf{p}^N, t) \equiv \rho(\mathbf{q}^N, \mathbf{p}^N, t) / M$, which represents the *fraction* of the ensemble (per unit volume) that are centered around $\mathbf{q}^N, \mathbf{p}^N$ at time t . The advantage of working with f is that it is normalized to unity:

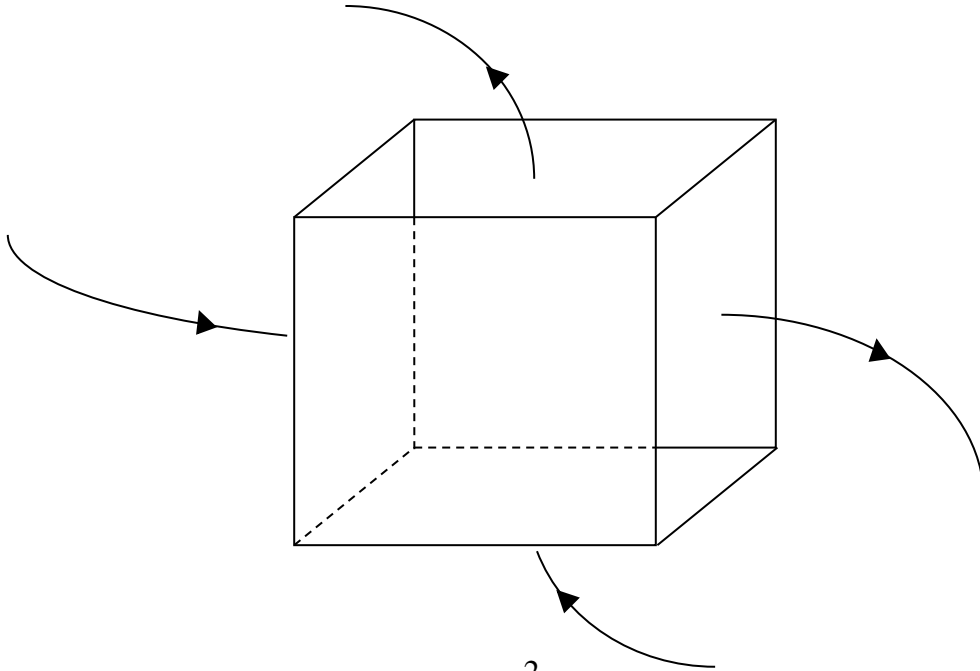
$$\int f(\mathbf{q}^N, \mathbf{p}^N, t) d\mathbf{q}^N d\mathbf{p}^N = 1 \quad (2)$$

and it can therefore also be interpreted as a probability density function.

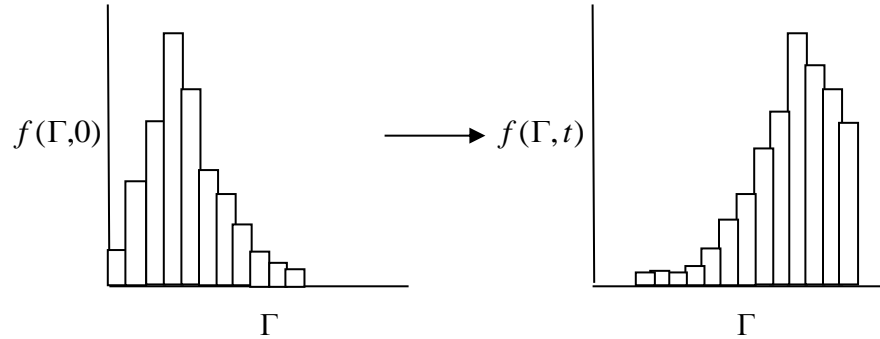
Now as time evolves, the positions and momenta of the phase points (i.e., microstates) surrounding $\mathbf{q}^N, \mathbf{p}^N$ will evolve too, in accordance with the Hamiltonian equations of motion:

$$\dot{q}_{i\alpha} = \frac{\partial H}{\partial p_{i\alpha}}, \quad \dot{p}_{i\alpha} = -\frac{\partial H}{\partial q_{i\alpha}}, \quad i = 1, 2, \dots, N, \quad \alpha = x, y, z \quad (3)$$

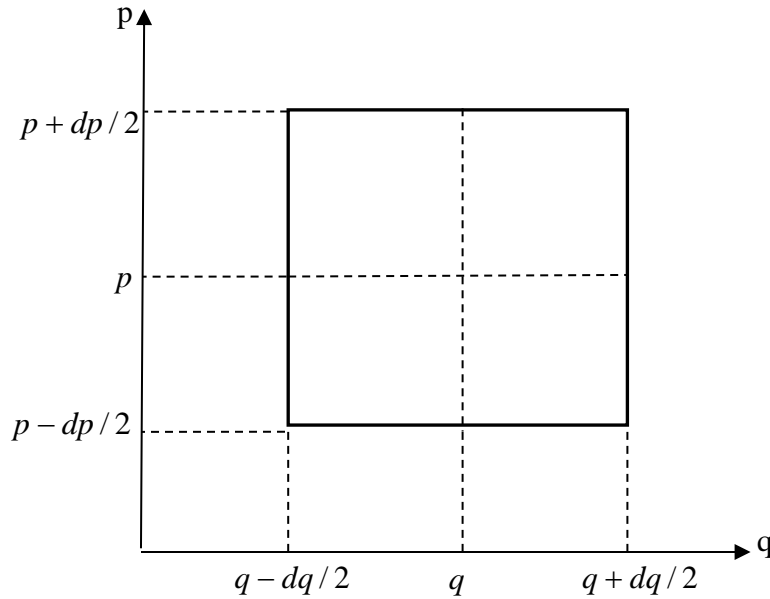
And as they follow their individual trajectories, some of them will enter the box (which itself remains stationary around $\mathbf{q}^N, \mathbf{p}^N$), and some will leave, changing the number that were there originally. The situation that has to be imagined looks a bit like this:



which might lead to a situation like this:



We'll now try and determine how the number of microstates in the given phase space volume element changes with time. For this purpose it helps to first consider a system consisting of just a single particle in 1-d. The phase space of this system is 2-dimensional, and a phase “volume” element in this space is a rectangular area. If the width of the rectangle along q is dq and that along p is dp , the relevant volume element is as shown below:



Now consider the left face of this rectangle where q has the value $q - dq/2$. In an interval of time dt , and for a given value of p , the number of systems in the ensemble that enter the rectangle through this face is

(density of phase points at $q - dq/2, p, t$) \times (width of face along p) \times (rate of change of q at $q - dq/2, p, t$) $\times dt$

$$\begin{aligned}
&= \rho(q - dq/2, p; t) \times dp \times \dot{q}(q - dq/2, p, t) \times dt \\
&\approx \left(\rho(q, p; t) - \frac{dq}{2} \frac{\partial \rho}{\partial q} + O(dq^2) \right) \times dp \times \left(\dot{q}(q, p, t) - \frac{dq}{2} \frac{\partial \dot{q}}{\partial q} + O(dq^2) \right) \times dt \\
&= \rho dp \dot{q} dt - \frac{1}{2} \rho dp dq \frac{\partial \dot{q}}{\partial q} dt - \frac{1}{2} dp dq \frac{\partial \rho}{\partial q} \dot{q} dt
\end{aligned} \tag{4}$$

In the same interval of time dt , and for the given value of p , some number of systems in the ensemble leave the rectangle through the opposite face, at $q + dq/2$. That number is

$$\begin{aligned}
&\rho(q + dq/2, p; t) \times dp \times \dot{q}(q + dq/2, p, t) \times dt \\
&\approx \left(\rho(q, p; t) + \frac{dq}{2} \frac{\partial \rho}{\partial q} + O(dq^2) \right) \times dp \times \left(\dot{q}(q, p, t) + \frac{dq}{2} \frac{\partial \dot{q}}{\partial q} + O(dq^2) \right) \times dt \\
&= \rho dp \dot{q} dt + \frac{1}{2} \rho dp dq \frac{\partial \dot{q}}{\partial q} dt + \frac{1}{2} dp dq \frac{\partial \rho}{\partial q} \dot{q} dt
\end{aligned} \tag{5}$$

So the net inflow of systems into the rectangle through these two opposite faces in dt is the difference between Eqs. (4) and (5), which is

$$dn_q = - \left(\rho \frac{\partial \dot{q}}{\partial q} + \dot{q} \frac{\partial \rho}{\partial q} \right) dp dq dt \tag{6}$$

In exactly the same way, we can determine the flux of systems entering the rectangle through the face $p - dp/2$ in the interval dt and at a given value of q , as well as the flux of systems leaving the rectangle through the opposite face $p + dp/2$ in the same interval of time and at the given value of q . And as a result of these fluxes, we find that the net number of systems dn_p that enter the rectangle along p in the interval of time dt is

$$\begin{aligned}
dn_p &= \rho(q, p - dp/2; t) \times dq \times \dot{p}(q, p - dp/2, t) \times dt \\
&\quad - \rho(q, p + dp/2; t) \times dq \times \dot{p}(q, p + dp/2, t) \times dt \\
&\approx \left(\rho(q, p; t) - \frac{dp}{2} \frac{\partial \rho}{\partial p} + O(dp^2) \right) \times dq \times \left(\dot{p}(q, p, t) - \frac{dp}{2} \frac{\partial \dot{p}}{\partial p} + O(dp^2) \right) \times dt
\end{aligned}$$

$$\begin{aligned}
& - \left(\rho(q, p; t) + \frac{dp}{2} \frac{\partial \rho}{\partial p} + O(dp^2) \right) \times dq \times \left(\dot{p}(q, p, t) + \frac{dp}{2} \frac{\partial \dot{p}}{\partial p} + O(dp^2) \right) \times dt \\
& = - \left(\rho \frac{\partial \dot{p}}{\partial p} + \dot{p} \frac{\partial \rho}{\partial p} \right) dp dq dt
\end{aligned} \tag{7}$$

Adding Eqs. (6) and (7), we get the *total* number of systems that enter the rectangle in the time dt . And the rate of change of this number with time is

$$\frac{\partial n_2}{\partial t} = - \left(\rho \frac{\partial \dot{q}}{\partial q} + \dot{q} \frac{\partial \rho}{\partial q} \right) dp dq - \left(\rho \frac{\partial \dot{p}}{\partial p} + \dot{p} \frac{\partial \rho}{\partial p} \right) dp dq \tag{8}$$

the subscript 2 denoting the fact that we're dealing with a phase space of 2 dimensions.

This 2-dimensional example should make it obvious what the corresponding result will be for a system consisting of N particles in 3 dimensions; it is

$$\frac{\partial n}{\partial t} = - \sum_{i=1}^N \left[\rho \left(\frac{\partial}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i + \frac{\partial}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i \right) + \dot{\mathbf{q}}_i \cdot \frac{\partial \rho}{\partial \mathbf{q}_i} + \dot{\mathbf{p}}_i \cdot \frac{\partial \rho}{\partial \mathbf{p}_i} \right] d\mathbf{p}^N d\mathbf{q}^N \tag{9}$$

where the dot products have their usual meaning.

Recall that the positions and momenta in the above equation are governed by Hamilton's equations, and so

$$\frac{\partial}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i + \frac{\partial}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i = \sum_{i=1}^N \sum_{\alpha} \left(\frac{\partial}{\partial q_{i\alpha}} \frac{\partial H}{\partial p_{i\alpha}} + \frac{\partial}{\partial p_{i\alpha}} \left(- \frac{\partial H}{\partial q_{i\alpha}} \right) \right)$$

which is 0 because mixed partial second derivatives are equal. Using this result in Eq. (9), along with Hamilton's equations, and then dividing both sides of the equation by $M d\mathbf{p}^N d\mathbf{q}^N$, we find the following result:

$$\frac{\partial f}{\partial t} = - \sum_{i=1}^N \sum_{\alpha} \left(\frac{\partial H}{\partial p_{i\alpha}} \frac{\partial f}{\partial q_{i\alpha}} - \frac{\partial H}{\partial q_{i\alpha}} \frac{\partial f}{\partial p_{i\alpha}} \right) \tag{10}$$

This is the Liouville equation, and it is one of the key equations of time-dependent statistical mechanics. It is usually written in the following operator form

$$\frac{\partial f}{\partial t} = -iL f \tag{11}$$

where i is the square root of -1, and L is the so-called Liouvillian, defined as

$$iL = \sum_{i=1}^N \sum_{\alpha} \left(\frac{\partial H}{\partial p_{i\alpha}} \frac{\partial}{\partial q_{i\alpha}} - \frac{\partial H}{\partial q_{i\alpha}} \frac{\partial}{\partial p_{i\alpha}} \right) \quad (12a)$$

L is purely imaginary. The factor of i in the definition of the Liouvillian is entirely a matter of convention, but its introduction makes it possible to connect with various results in quantum mechanics. Equation (12a) is also often rewritten in the following shorthand notation:

$$\begin{aligned} iL &= \sum_{i=1}^N \left(\dot{\mathbf{q}}_i \cdot \frac{\partial}{\partial \mathbf{q}_i} + \dot{\mathbf{p}}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) \\ &\equiv \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} \end{aligned} \quad (12b)$$

We'll soon use the Liouville equation in the averages that define time correlation functions, but before we do that, we'll quickly derive an equation in f that gives us an idea of what its time evolution physically means. For this purpose, consider Eq. (10), and rewrite it as follows:

$$\frac{\partial f}{\partial t} + \sum_{i=1}^N \left(\mathbf{q}_i \cdot \frac{\partial f}{\partial \mathbf{q}_i} + \mathbf{p}_i \cdot \frac{\partial f}{\partial \mathbf{p}_i} \right) = 0 \quad (13)$$

Now recall that $f = f(\mathbf{q}^N, \mathbf{p}^N, t)$, so if we make infinitesimal changes to the independent variables in this relation, we find that

$$df = \sum_{i=1}^N \left(\frac{\partial f}{\partial \mathbf{q}_i} \cdot d\mathbf{q}_i + \frac{\partial f}{\partial \mathbf{p}_i} \cdot d\mathbf{p}_i \right) + \frac{\partial f}{\partial t} dt \quad (14)$$

If we divide this equation by dt and then use Eq. (13) in the result, we end up with

$$\frac{df}{dt} = 0 \quad (15)$$

This tells us that the fractional phase space density in the neighbourhood of any selected *moving* phase point is a constant along the trajectory of that phase point (McQuarrie.) So the cloud of phase points moves like a flowing incompressible liquid. Note that the partial derivative of f with respect to t , $\partial f / \partial t$, is not 0, meaning at a *fixed* location in phase space f can change its value.

- Time Evolution of Dynamical Variables

Having found how the density distribution function f evolves in time, we're now in a position to determine how dynamical variables evolve in time. But we first need to understand a few other things about the Liouville equation and the Liouville operator. Recall that

$$\frac{\partial f}{\partial t} = -iL f$$

Now if L were an algebraic quantity, independent of t , we could easily solve the above equation for a definite interval of time between, say, $t = 0$ and $t = t$; the solution would read

$$f(t) = e^{-iLt} f(0) \quad (16)$$

where $f(t) \equiv f(t; \Gamma)$ and $f(0) \equiv f(\Gamma)$. Even though L is actually an operator, we'll continue to regard Eq. (16) as the *formal* solution of the Liouville equation, with the understanding that e^{-iLt} is always to be interpreted in terms of the series expansion of the exponential. In other words,

$$e^{-iLt} \equiv \sum_{n=0}^{\infty} \frac{1}{n!} (-iLt)^n \quad (17)$$

With this understanding, we can write down some formal expressions for the time dependence of dynamical variables. Consider one such variable, say, B . We'll assume that B is not explicitly a function of time, but depends on time through its dependence on positions and momenta. So, in general, we can write

$$B(t) = B(\mathbf{q}^N(t), \mathbf{p}^N(t)) \equiv B(\Gamma(t))$$

If we now use the chain rule to differentiate this equation with respect to time, we obtain

$$\frac{\partial B(t)}{\partial t} = \dot{\Gamma} \cdot \frac{\partial B(t)}{\partial \Gamma}$$

where we defined the operator $\dot{\Gamma} \cdot \partial / \partial \Gamma$ in (12b). Referring to that equation, we see that

$$\frac{\partial B(t)}{\partial t} = iLB(t) \quad (18)$$

and so formally,

$$B(t) = e^{iLt} B(0) \tag{19}$$

where $B(t) = B(t; \Gamma)$ and $B(0) = B(\Gamma)$.

Equations (16) and (19) will be important in the derivation of expressions for phase space averages of dynamical variables.